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A MEMORANDUM REPORT

PHYSICAL CONSTANTS OF MCE

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Member Classified Documents Review Committee
NOV 21 1955

by

B. L. Harris,
Captain, C.W.S.

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Project: A 1.13
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A MEMORANDUM REPORT

PHYSICAL CONSTANTS OF MCE

By

B. L. Harris, Capt., CWS

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ABSTRACT

OBJECT:

The object of Project A 1.13, Agent MCE and Related Compounds, is to study MCE and MFI and their analogs with a view to estimating their effectiveness as CW agents.

The object of the work described in this report was to measure the various physical constants of MCE, particularly the vapor pressure-temperature relationship, in order to make these data available to investigators working on the various phases of this project.

RESULTS:

The physical constants of MCE are as follows:

n_D^{20}	1.4240
Formula weight	162.3
Parachor (25°C.)	359.8
Freezing point (purest sample)	-50.0°C.
Boiling point (extrapolated from vapor pressure data)	246°C.
Heat of vaporization Average values 35-95°C.	12900 cal./mol. or 79.6 cal./gram.

Temp. °C.	Vapor Pressure mm. Hg	Volatility mg./l.	Density g./ml.	Viscosity centistokes	Viscosity centipoises	Surface Tension dynes/cm.
-10	-	-	1.105	-	-	-
0	-	-	1.096	-	-	-
10	-	-	1.087	3.00	3.26	-
15	-	-	1.082	-	-	-
20	0.0483	0.429	1.077	-	-	-
25	0.0701	0.612	1.073	2.19	2.35	32.0
30	0.100	0.858	1.068	-	-	31.8
35	0.142	1.20	1.064	1.67	1.78	-
45	0.275	2.25	-	-	-	-

The vapor pressure - temperature relationship is as follows:

$$\log_{10} p = 8.305 - \frac{2820}{T}$$ where p = vapor pressure, mm. Hg. T = temperature, °K.

The expansion to 65°C., and the density of crude MCE tapped from a 250 kg. bomb, were measured, and are in table 4.

CONCLUSIONS: None.

RECOMMENDATIONS: None

TABLE OF CONTENTS

[redacted]

PHYSICAL CONSTANTS OF MCE

PROJECT: A 1.13 T.D.M.R. 1094

I. INTRODUCTION. [redacted]

A. Object.

The object of Project A 1.13, Agent MCE and Related Compounds, is to study MCE and MFI and their analogs with a view to estimating their effectiveness as CW Agents.

The object of the work described in this report was to measure the various physical constants of MCE, particularly the vapor pressure - temperature relationship, in order to make these data available to investigators working on the various phases of this project.

B. Authority.

The authority for the work described in this report is Project A 1.13 of the Project Program for Fiscal Year 1946.

II. HISTORICAL.

Early in the spring of 1945 a number of captured German bombs and shell were received at Edgewood Arsenal. When one of each was tapped, both proved to contain crude MCE. The bomb was the 250-kg. size, and contained MCE with approximately 5% of monochlorobenzene. The shell (105-mm. howitzer) contained MCE with about 20% of monochlorobenzene. Samples of these materials were distilled by personnel in the Chemical Division to obtain the pure agent for study. Tests are now in progress on various phases of this study, and in order to supply background data for the testing and evaluation of the agent, the physical constants were determined and are reported here.

III. EXPERIMENTAL.

A. Materials and Equipment.

1. MCE.

A number of samples of pure (twice-distilled) MCE and one sample of the crude material from the bomb were used in this work. In addition, one sample of material synthesized at this Arsenal by Capt. Rueggeberg (report in progress) was used. The results of analysis of the pure samples are given in table 1.

Table 1

Analyses of Pure MCE Samples Used For Determinations of Physical Constants

Sample No.	Calc.	Found M1063	M1067	M1078	M1081	S-184*
CN as HCN, %	16.04	16.07	15.78	15.45	16.19	16.23
Nitrogen, %	17.28	16.98	17.00	16.65	16.78	17.05
Phosphorus, %	19.10	19.04	19.04	19.12	18.76	-
n_D^{20}	-	1.4239	1.4243	1.4239	1.4240	1.4240
n_D^{30}	-	1.4190	1.4185	1.4197	1.4200	-
Chlorine	-	-	-	-	0.12	nil

* This sample was synthesized at Edgewood Arsenal. The others were material twice distilled from that in the 250-kg. bomb.

2. Equipment.

The equipment is described under the separate tests in Section III C, below.

B. Procedure.

The various procedures are described in Section III C, below.

C. Results.

1. Vapor Pressure, Volatility, and Heat of Vaporization.

a. Transference Method.

The vapor pressure was measured at 25-55°C. in a vapor-transference apparatus, by bubbling nitrogen at measured pressure through the agent in a triple-pass bubbler immersed in a water thermostat. The procedure has been described in detail in numerous reference texts. The specific apparatus and its manipulation have been completely discussed by Pecorella and Macy (1). The values obtained at first were erratic, due to the difficulty of weighing the small quantities evaporated as a result of the low vapor pressure of the agent and the short time of the run, and so were discarded. The later values were obtained by allowing the apparatus to run for 2 to 4 days at a time but even so the values at 25°C. were not consistent. The experimental values so obtained are given in table 2. Two samples of MCE were used for the determinations, which are corrected to mm. of Hg. at 0°C.

Table 2

Experimental Values of Vapor Pressure of MCE by the Air Transference Method

Temp. °C.	Wt. loss of MCE g.	Vol. of Nitrogen ml.	Pressure of Nitrogen mm.Hg.	Vapor Pressure Sample M1063 mm. Hg.	Vapor Pressure Sample S-184 mm. Hg.	Average* mm.Hg.
25.0	0.0095	21980	760.0	0.0454		
	0.0137	25610	760.0	0.0561		
	0.0202	26640	760.6	0.0796		
	0.0118	28620	761.2	0.433		-**
35.0	0.0287	20260	746.0	0.146		
	0.0292	20010	744.6	0.150		
	0.0236	17125	759.5		0.144	0.146
45.0	0.0235	9720	760.0	0.254		
	0.0342	14880	760.5	0.243		
	0.0505	21320	761.6	0.249		
	0.0342	11600	742.0	0.270		
	0.0257	10060	761.5		0.268	0.261
55.0	0.0355	6520	763.7		0.573	
	0.0385	8310	762.5		0.487	0.530

* The average values were obtained by averaging the determinations for each sample separately, and then averaging those values.

** No average was calculated due to the inconsistency of the data.

b. Ramsay-Young Method.

This method is likewise a standard one described in a number of texts. The assembly of apparatus used for the work here was taken directly from Reilly and Rae (?). The essential feature was a thermometer, the bulb of which was wrapped with absorbent cotton kept wet with the agent by means of a dropping funnel, placed in an evacuated chamber immersed in a water thermostat. It was operated by evacuating the chamber to a measured pressure, allowing time for ecuilibrium, and reading the temperature. It was found that, due to the low vapor pressure of this agent, reliable results could only be obtained if the temperature and pressure were held constant for about an hour. Only two values were obtained by this method, as follows:

Temperature	Vapor Pressure
68.9°C.	1.15 mm. Hg.
93.3°C.	3.7 mm. Hg.

c. Distillation Data.

The apparatus used by Rueggeberg to distill sample S-184 and one other only slightly less pure sample was one in which the manometer was connected to the point in the system at which the temperature was read. The distillation temperature-pressure data were, in effect, vapor pressure data, and are included in the values reported here as follows:

Temperature	Vapor Pressure
72.5-73°C.	1.5 mm.
86-87 (mostly 87)°C.	3 mm.

d. Average Values of Vapor Pressure, Volatility and Heat of Vaporization.

The values reported above for the vapor pressure were averaged on a log p vs. 1/T plot by the method of least squares to give the following equation:

$$\log p = 8.305 - \frac{2820}{T}$$

where log p = logarithm to the base 10 of the vapor pressure in mm. Hg.
T = absolute temperature, °K.

The values calculated from this equation are given in table 3. The check was quite good, as comparison with table 2 or reference to figure 1 will show.

The volatility of the MCE was calculated from the calculated values of vapor pressure by the ideal gas law and the values are given in table 3.

The boiling point at atmospheric pressure (760 mm. Hg.) was likewise calculated from the equation above, assuming the plot of log p vs. 1/T was linear to so high a value; the value so obtained was 246°C.

Table 3

Vapor Pressure of MCE Calculated from the Experimental Data by Method of Least Squares

$$\log p = 8.305 - \frac{2820}{T}$$

Temperature °C.	Vapor Pressure mm. Hg.	Volatility mg./l.
20	0.0483	0.429
25	0.0701	0.612
30	0.100	0.858
35	0.142	1.20
45	0.275	2.25
246.3*	760	-

* Normal boiling point, assuming the equation holds to 760 mm. Hg.

The heat of vaporization was calculated from the modified Clapeyron-Clausius equation:

$$\frac{d \ln p}{dT} = \frac{Hv}{RT^2}$$

where ln p = logarithm to the base e of the vapor pressure
Hv = heat of vaporization, cal./mol.
R = gas constant, 1.987 cal./°C./mol.

Using the equation for the vapor pressure of MCE

$$\log p = 8.307 - \frac{2820}{T}$$

or $$\ln p = 2.303 \left(8.307 - \frac{2820}{T}\right)$$

$$\frac{d \ln p}{dT} = 2.303 \times \frac{2820}{T^2} = \frac{Hv}{RT^2}$$

$$Hv = 2.303 \times 2820 \times R = 12,900 \text{ cal./mol.}$$

and the heat of vaporization per gram = 12,900 ÷ 162.3 = 79.6 cal./gram

It will be noted that these are the average values of heat of vaporization over the range of the experimental data.

2. Density of Pure and Crude MCE.

The density of both the pure MCE and the crude MCE from the 250-kg. bomb was measured at various temperatures by dilatometer. The values are given in table 4. Also included are the values for the percent expansion from various temperatures to 65°C., for use in filling calculations. The plot of density versus temperature was linear over the range studied.

Table 4

Density of Pure and Crude MCE

Temp.	Pure MCE (Sample M1067)			Crude MCE (From 250-kg. bomb.)		
	Exptl. Values	Values from plot	Expansion* to 65°C.	Exptl. Values	Values from plot	Expansion* to 65°C.
°C.	g./ml.	g./ml.	%	g./ml.	g./ml.	%
-10		1.105	6.65		1.118	6.48
0		1.096	5.79		1.109	5.62
10	1.0869(9.8°C)	1.087	4.92	1.1001(9.8°C)	1.100	4.76
15		1.082	4.44		1.095	4.29
20		1.077	3.96		1.091	3.90
25	1.0731(24.9°C)	1.073	3.57	1.0864(24.9°C)	1.086	3.43
30		1.068	3.09		1.082	3.05
35	1.0636	1.064	2.70	1.0771	1.077	2.57
65		1.036			1.050	

* These values are reliable to two significant figures.

3. Freezing Point.

The freezing point of two samples of MCE was determined by Beckmann technique using a toluene filled thermometer which was correct at -45.2°C. (f.p. of monochlorobenzene). Each determination was run in duplicate. It was found that the material was difficult to freeze unless a few particles of a drying agent (Drierite) were added. The values obtained were as follows.

Sample	Freezing Point Obtained	Average Freezing Point
M1078	-51.0; -50.8	-50.9°C.
S 184	-50.0, -50.0	-50.0°C.

The Sample S 184 seemed to be somewhat more pure, on the basis of the higher freezing point, as well as on the basis of analysis (table 1)

4. Viscosity.

The viscosity of pure MCE was measured by Cannon Fenske-Ostwald viscometer, at various temperatures. The experimental values are given in table 5. Each value is the average of 3 5 separate determinations:

Table 5

Viscosity of Pure MCE

Temperature	Viscosity	
°C.	Centistokes	Centipoises
10.0	3.00	3.26
25.0	2.19	2.35
35.0	1.67	1.78

[redacted]

5. Surface Tension.

The surface tension was determined on pure sample M10R1 using a du Nouy interfacial tensiometer calibrated by the method of Macy (3). The values were found to vary little with temperature, as follows:

Temperature	Surface Tension
25.0°C.	32.0 dynes/cm.
30.0°C.	31.8 dynes/cm.

IV. DISCUSSION.

The parachor of MCE was calculated from the density and surface tension. In effect, this constant is a corrected molar volume =

$$P = MS^{1/4} = \frac{\text{molecular weight}}{d} S^{1/4}$$

where P = Parachor

M = molar volume

S = surface tension, dynes/cm.

d = density, g./ml.

The value calculated for MCE using the values of d and S at 25°C., was 359.8. The calculated value using Parachor equivalents tabulated by Glasstone (4) and Mumford and Phillips (5) was 357.3. The agreement was fair and so confirms the known structure of the material.

The refractive indices were determined on these samples by the Analytical Branch, as a control property. The values at 20°C. for the sodium D line were in good agreement (table 1) for all the samples, giving an average figure of 1.4240. The values at 30°C. were discordant due to difficulties of temperature and humidity control.

V. CONCLUSIONS. None.

VI. RECOMMENDATIONS. None.

VII BIBLIOGRAPHY.

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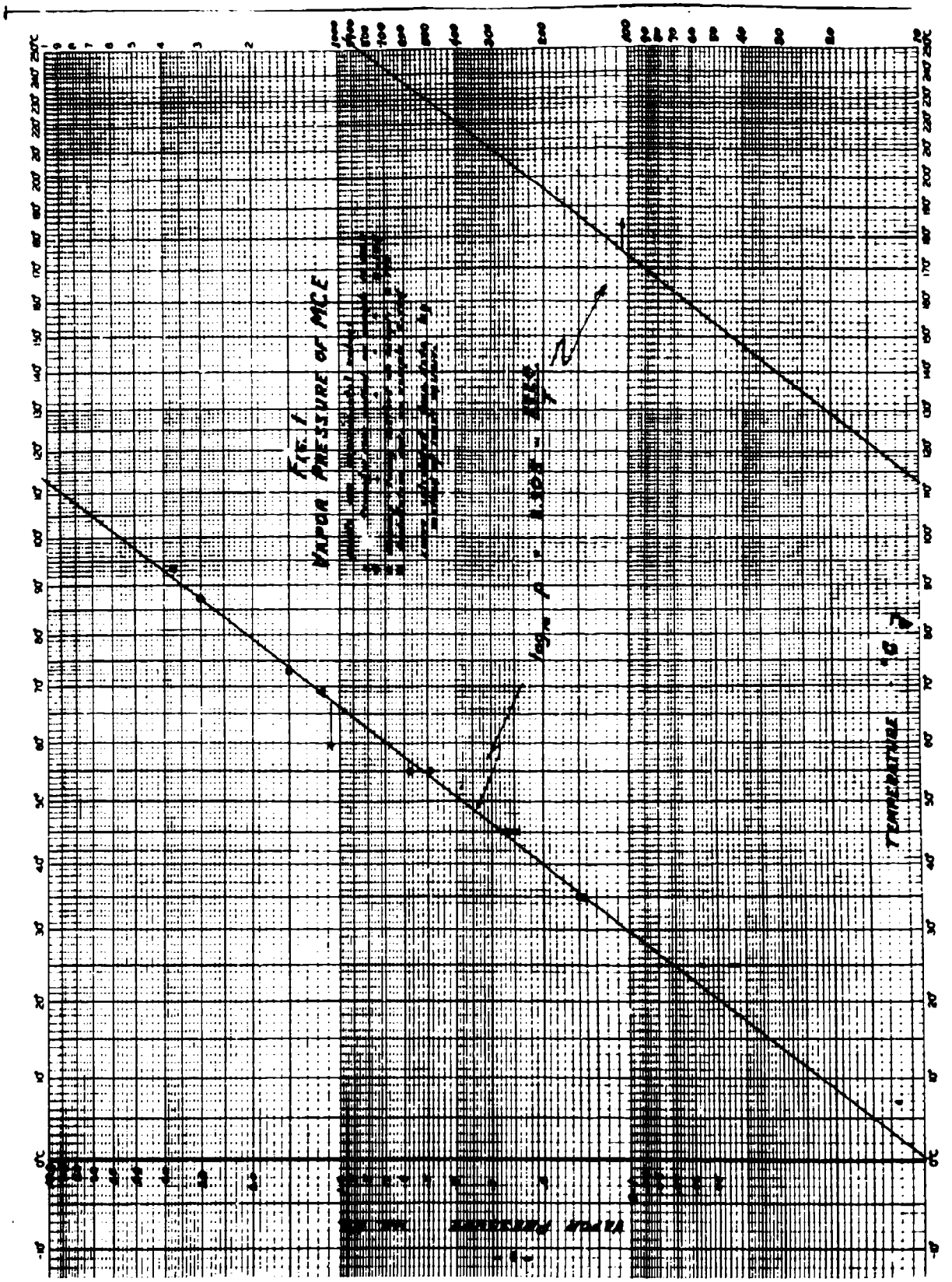

T.D.M.R. 1094

Project: A 1.13

Notebook No. 2363

Experimental Work:
Started: 11 May 1945
Completed: 4 July 1945
(intermittent)

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US ARMY RESEARCH, DEVELOPMENT AND ENGINEERING COMMAND
EDGEWOOD CHEMICAL BIOLOGICAL CENTER
5183 BLACKHAWK ROAD
ABERDEEN PROVING GROUND, MD 21010-5424

REPLY TO
ATTENTION OF

MAY 20 2015

RDCB-DPS-RS

MEMORANDUM THRU Director, Edgewood Chemical Biological Center, (RDCB-D/Dr. Joseph Corriveau), 5183 Blackhawk Road, Aberdeen Proving Ground, Maryland 21010-5424

FOR Defense Technical Information Center, 8725 John J. Kingman Road, Ft Belvoir, VA 22060

SUBJECT: Internal Request for Change in Distribution

1. This action is in response to an Edgewood Chemical Biological Center (ECBC) Internal Request for a Change in Distribution for the following documents:

a. Investigations on MCE and MFI, 28 Sep 45, MIT, Cambridge, MA, **CBRNIAC-CB-177091.**

b. Toxicity and Irritancy of Chemical Agents, 15 May 45, National Defense Research Committee, Wash. DC, **CBRNIAC-CB-182867**.

c. Physical Constants of MCE, 16 Jul 45, Edgewood Arsenal, APG, MD **CBRNIAC-CB-010375**. AD B964103

d. Thermal Studies on MCE, 19 Sep 45, Edgewood Arsenal, APG, MD, **CBRNIAC-CB-010374.**

2. The listed documents have been reviewed by ECBC Subject Matter Experts and deemed suitable for the change in distribution to read "Approved for public release; distribution unlimited."

3. The point of contact is Adana Eilo, ECBC Security Specialist, (410) 436-2063 or adana.l.eilo.civ@mail.mil.

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